REACTION OF 2-FURYL-PROPYLKETONE WITH AMMONIA

REACTION OF 2-FURYL-PROPYLKETONE WITH AMMONIA*

By

Hiroshi SUGISAWA, Hironari SUGIYAMA and Kiyoshi ASO

Department of Agricultural Chemistry, Faculty of Agriculture, Tohoku University, Sendai, Japan

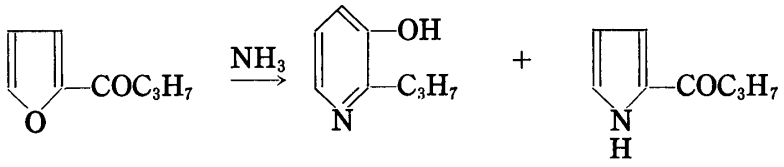
(*Received November 1, 1959*)

It was previously reported (1) that 2-alkyl-3-hydroxy-pyridines and 2-alkyl-pyrrylketones were formed from 2-furyl-alkylketones by heating with ammonia in an autoclave.

Preparation of 2-propyl-3-hydroxy-pyridine from 2-furyl-propylketone was reported by Gruber (2). The formation mechanism of 2-alkyl-3-hydroxy-pyridines from furan derivatives was proposed as an ammonolytic cleavage by Gruber (2) and Leditischke (3), and their investigation in that procedure dealt almost exclusively with the formation of 2-alkyl-3-hydroxy-pyridines, they did not mention the formation of 2-alkyl-pyrrylketones.

We have found that it is possible to obtain in good yield both 2-alkyl-3-hydroxy-pyridines and 2-alkyl-pyrrylketones by similar reaction, however, it was uncertain whether the reaction is ammonolytic cleavage (2, 3) or some other competitive reaction. In a previous work (1), 2-furyl-alkylketones having methyl or ethyl group in side chain were used as starting material, but one object of this investigation is to prove the formation mechanism, so it was neccessary to carry out the same reaction in condition of extended side-chain, the next investigation was on a similar reaction in the hope that 2-propyl-3-hydroxy-pyridine and 2-propyl-pyrrylketone might be synthesized from 2-furyl-propylketone, and these were obtained by reacting 2-furyl-propylketone with ammonia under the same condition as mentioned previously.

Now, we would like to report the findings of this investigation in the following.



(I) (II) (III)

* This work was published as the reaction of furan derivatives with ammonia (V).

Experimental

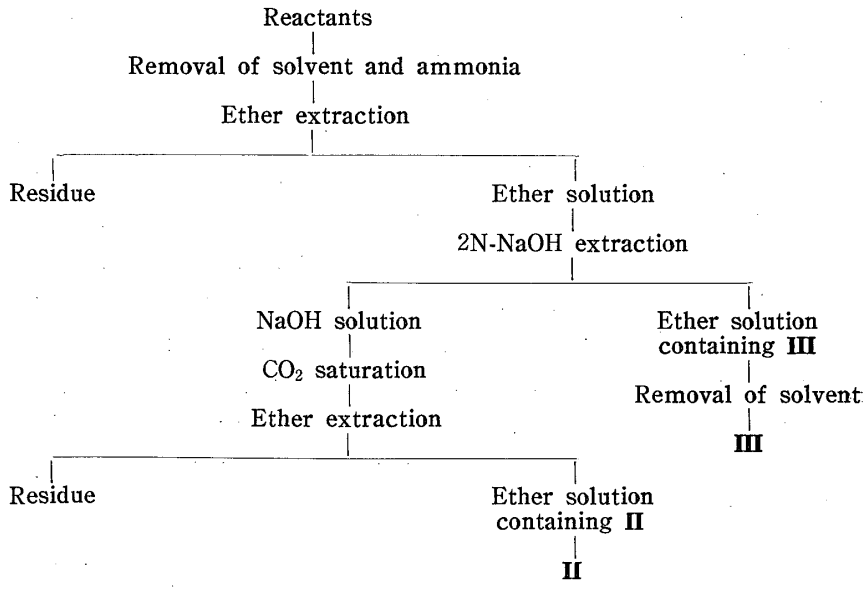
1) *2-Furyl-propylketone* (I).

2-Furyl-propylketone was prepared by Friedel-Crafts reaction using boron-trifluoride as a catalyst. Furan 16 g (0.23M), *n*-butylic anhydride 50 g (0.48M) were placed in a three-neckflask and well stirred under anhydrous condition for 10 min at 0°C. Addition of 5*ml* of boron-trifluoride etherate caused a slight rise of temperature. The mixture was kept at 15°C, after well stirring for 1.5 hr, 100 *ml* of water was added to the reaction mixture. The ketone was taken up with ether, washed with Na_2CO_3 solution, and then dried over anhydrous Na_2SO_4. After removal of the solvent, 24 g of crude ketone was distilled under reduced pressure, bp_{17} 90–95°C.

2) *Isolation of 2-propyl-3-hydroxy-pyridine* (II) *and 2-propyl-pyrrylketone* (III).

The reactants as shown in the Table 1 were heated in an autoclave at 180°C for 20 hr, and cooled. After removal of the solvent and ammonia under reduced pressure, the residue was taken up with ether. Ether solution containing II and III was extracted to isolate II with 2N-NaOH, III remained in the ether solution, and NaOH solution was saturated with CO_2 and then extracted again with ether for 48 hr. II was obtained from the ether extract.

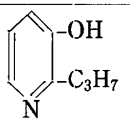
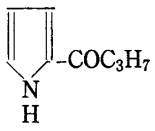
The isolation method of II and III is shown in the following.



3) *2-Propyl-3-hydroxy-pyridine* (II).

II was purified by the method of sublimation under reduced pressure, colorless prism, mp 133–134°C. The yield of II is shown in Table 1. Anal. Found C, 70.35; H, 8.10; N, 10.57% Calcd. for $C_8H_{11}NO$ C, 70.04; H, 8.08; N, 10.21%. II indicated a deep red color by $FeCl_3$ solution, and a deep green color by the Folin-Denis reagent. This melting point was identical with that of 2-

Table 1.

Reactants	Yield % (theoritical)	
		
Furyl-propylketone 2g, Liq. NH_3 10*ml*, MeOH 10*ml*.	30	28
Furyl-propylketone 2g, Liq. NH_3 10*ml*, NH_4Cl 0.5g	15	15
Furyl-propylketone 2g, MeOH 20*ml*, 28% NH_4OH 20*ml*	48	40

propyl-3-hydroxy-pyridine described by Gruber (2). Ultra-violet spectrum of **II** is shown in the Fig. 1, λ_{max} 283 mμ.

When the infrared spectrum of **II** was compared with our findings described previously (1), **II** has the characteristic absorption bands as shown in the

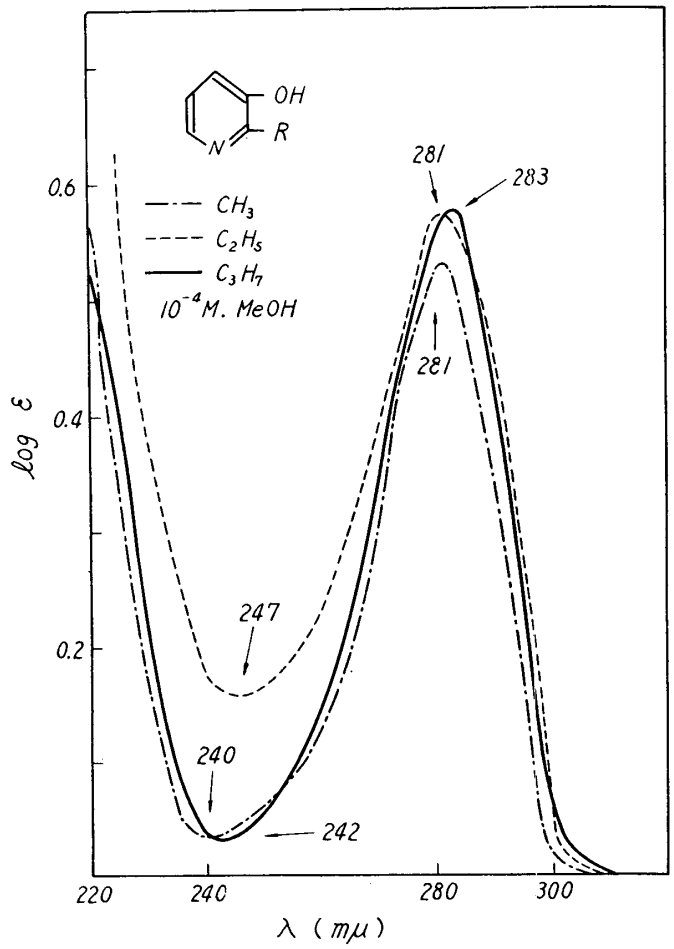


Fig. 1. Ultra-violet spectrum of 2-alkyl-3-hydroxy-pyridines.

following (in cm^{-1}), cyclic C=N 1575, $-CH_3$ and $-CH_2$ 1455 and 1385, propyl group 742, 3-pyridol near 800, and also showed the hydroxyl group to be present in bonded form since it has two very broad bands centred at 2480~2490 and 1810. OH-N intermolecular hydrogen bond existed and this accounted for the wide spread for absorption.

Its picrate was prepared by the usual method, recrystallized from hot-water, yellowish needle, mp 112-3°C. Anal. Found N, 15.17% Calcd. for $C_{14}H_{14}N_4O_8$ N, 15.30%.

4) *2-Propyl-pyrrylketone* (**III**).

III was recrystallized from hot-water after sublimation, colorless needle, mp 48°C. This melting point was identical with that of 2-propylpyrrylketone reported by Oddo (4). Anal. Found C, 70.14; H, 8.11; N, 9.99% Calcd. for $C_8H_{11}NO$ C, 70.04; H, 8.08; N, 10.21%. The yield of **III** is shown in the Table 1. Ultra-violet spectrum of **III** is shown in the Fig. 2, λ_{max} 288 mμ. The infrared spectrum of **III** is shown in Fig. 4, and shows the characteristic

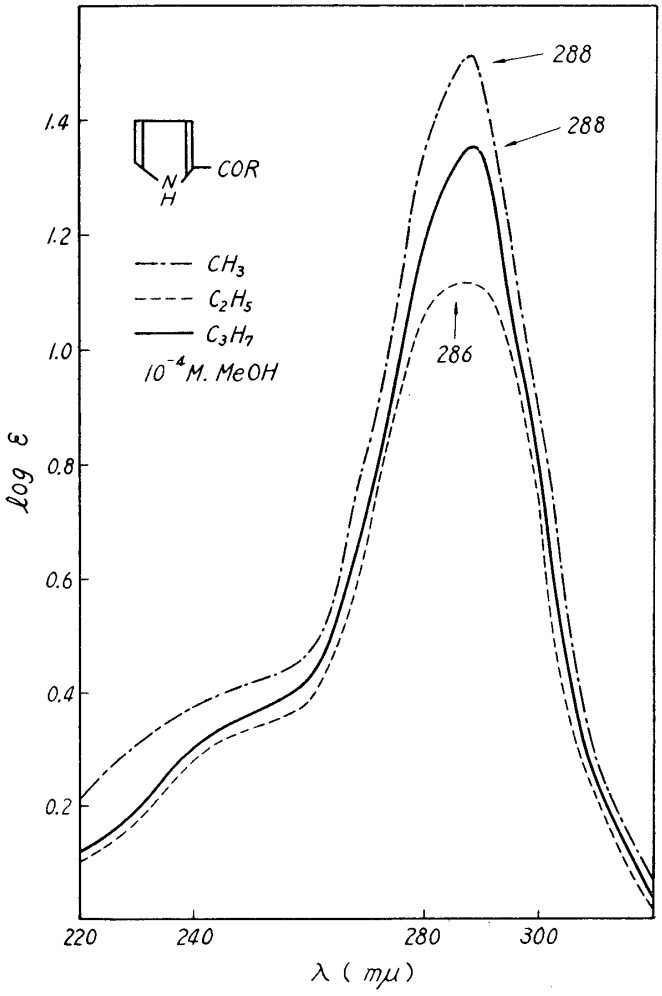


Fig. 2. Ultra-violet spectrum of 2-alkyl-pyrrylketones.

absorption bands as following (cm^{-1}), NH streching vibration band at 3300, band of carbonyl group 1640, NH deformation band 1550, $-CH_3$ and $-CH_2$ 1455 and 1383, propyl group 740.

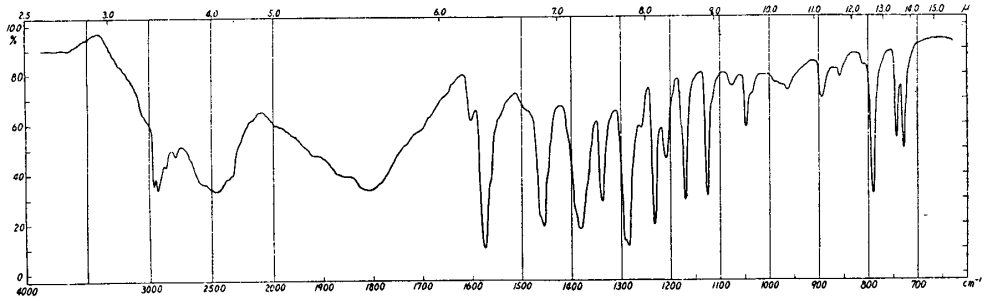


Fig. 3. Infrared spectrum of 2-propyl-3-hydroxy-pyridine (**II**).

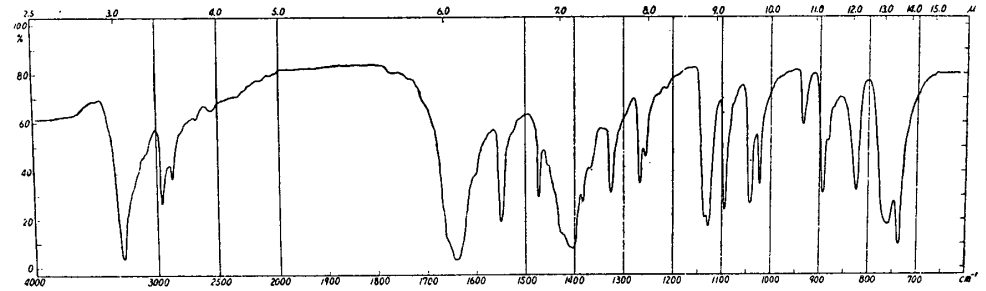


Fig. 4. Infrared spectrum of 2-propyl-pyrrylketone (**III**).

Summary

There was obtained in good yield 2-propyl-3-hydroxy-pyridine and 2-propyl-pyrrylketone by reacting 2-furyl-propylketone with ammonia at 180°C under several conditions as shown in the Table 1.

Acknowledgement

Thanks are due to the Microanalyzer of the Department of Chemistry, Tohoku University and the Spectral Operator of the Chemical Research Institute of Non-Aqueous Solution, Tohoku University for their technical assistance.

References

1) Sugisawa, H., and Aso, K. (1959). Tohoku J. Agr. Res., **10**, 137.
2) Gruber, W. (1953). Can. J. Chem., **31**, 664.
3) Leditischke, H. (1952). Ber., **85**, 202.
4) Oddo, B. (1910). Ber., **43**, 1012.